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(56) Documents cited
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(71) Applicant
Antony Grinham, 28 Harold Road, Braintree, Essex
(72) Inventor
Antony Grinham
(74) Agent
M. Dean, 140 Edgwarebury Lane, Edgware, Middlesex HA8 8NE

(54) Cement composition

(57) A cement composition which may be made into a mould with improved refractory and shrink-resistant properties and more easily drilled comprises high alumina cement, aggregate and clay. The aggregate may be sand and/or a refractory aggregate e.g. malachite. The mould may be used for thermo-forming or for dental purposes or the composition may be used to form a building material.

SPECIFICATION
Cement compositions

This invention relates to cement compositions. The invention was developed in relation to moulds but has other applications. The invention extends to mixes for use in making moulds, methods of making a mould from such a mix, moulds so made, processes using such moulds and articles made using such moulds.

Suitable materials for use in the manufacture of vacuum moulds are epoxy resins. However, these are very expensive. As a substitute, there was tried what is called "ordinary Portland cement" but this proved technically unsuitable. There was then tried a simple mould material made of one part of cement and three parts of sand. Water was added at the time of mixing to give workability. The product was suitable in some respects but had the disadvantage of being unsuitable for drilling.

The inventor of the present invention discovered that the reason for this unsuitability was that the drill gouged out particles of sand and therefore removed more material than was required. He further discovered that this problem could be avoided by including in the mix a relatively soft material into which the drill could press peripheral particles of sand. In experiments, the best such matrix material he found (i.e. the one giving the best drilling properties in the resulting mould) was clay.

Thus according to one aspect of the invention there is provided a composition comprising high alumina cement, aggregate (e.g. sand) and a soft matrix material, preferably clay. The sand gives the material strength and helps to prevent shrinkage. The high alumina content of the cement produces a gel which lines the mould and produces a smoothness at the surface which makes for good reproduction. It also improves the refractory properties of the resulting mould.

The mix so formed is improved by adding to it a refractory aggregate. The best one found is malachite. This increases the temperature range of the resulting mould (which can be further increased by omitting some or all of the sand or other non-refractory aggregate) and appears to help substantially to prevent the mould from shrinking when being formed. It also reduces or prevents cracking at high temperatures. Other aggregates that were tried were (non-refractory) industrial talc and whiting (chalk) and more successfully (refractory) firebrick but these produced nothing like the improvement that was obtained with malachite.

The high alumina cement used is any one conforming to British Standard B.S. 915, which *inter alia* has an alumina content of at least 39% w/w. For high temperature work with the resulting mould it may be necessary to use a cement higher in alumina content than 39% and cement with an alumina content of 70% w/w or even 80% w/w have been used successfully.

The malachite is preferably one with a low iron content of about 0.75% w/w, a high inherent alumina content of around 40%—42% w/w and a small particle size of about 75 microns grade, such as is available for example under the trade name Malachite 200, 75 micron grade (made by English China Clays Limited) from Fordamin Company Sales Limited, No. 3 Wharf, Brighton Road, Shoreham-by-Sea.

The clay should be that known in the trade as Grade C or finer (the finer it is the dryer it can be made, which is considered to give better properties to the mix). 300 microns is about the maximum useful size on this basis and is preferred because finer grades, through dryer, are more expensive.

The sand can be anything less than 600 microns grade, preferably a 300 micron grade or, more preferably, what is commonly called 90—150 micron grade.

Useful mixes have been made up with the following proportions by weight: cement 25% to 75% though preferably 45% to 55%; sand 5% to 70%, though preferably 15% to 40%; clay 5% to 30%, though preferably 5% to 15%; and malachite, is used, 10% to 35%, better 15% to 30%, and preferably 20% to 25%. The properties of the mixes were found to be better in the preferred ranges. As an example, an optimum mix combining reasonable cost with good refractory properties and good resistance to shrinkage has the following composition w/w:—

25%	sand E, 90—150 micron grade.
47.5%	high alumina cement conforming to B.S. 915 with alumina content about 39%.
22.5%	Malachite 200, 75 micron grade.
5%	clay, grade C.

Almost as good mixes were obtained by varying inversely the proportions of cement and sand as far as 20% cement and 52.5% sand, the proportion in each case being about 72.5% of the two ingredients combined.

In making a mould out of the mix, water is added to cause the ingredients to adhere and the mix to set. The water also gives workability and placing ease (ease of removing air bubbles). The water also contributes to the final strength of the mould. For every 100 parts by weight of the mix there are required some 10 to 50 (preferably 15 to 25) parts by weight of water. The exact quantity will depend on the mix being used and the degree of workability. In the case of the example given above, a suitable quantity of water is 20 parts for 100 parts of mix.

The mould is produced and used in any suitable manner. For example, for a telephone casing, an internal form is made, e.g. by being carved out of wood, a sheet of plastic is vacuum formed over this and the wood removed, water is added to the mix according to the example given above and this is put into the plastic sheet in place of the wood, this hardens to form a mould from which the plastic sheet is removed and onto which plastic can be heat formed into telephone casings.

The only comparable moulding material at the moment is thought to be epoxy resin. Moulding materials embodying the invention are far cheaper than epoxy resin, are far easier to use because they do not stick to the hands, they are less dermatitic, they are non-toxic and can be disposed of easily without fear of degrading to give off toxic fumes, there is less wastage since it is not necessary to mix excessive quantities of two materials as is required with epoxy resins.

Moulds produced from compositions embodying the invention have a high resistance to shrinkage and good heat resistant properties. Such a composition is therefore highly suitable for use in the thermo-forming industry. However, it will be apparent that many other fields are open to it. For example, the composition can be used as a replacement for dental plaster. Its main advantage in this field is that the mould can be repeatedly used on high temperature work as it has good stability under repeated cycles of firing and being returned to ambient temperature. The material is particularly suitable for this purpose because of the excellent surface produced by the gel referred to above due to the high alumina cement. This allows small peculiarities of shape, which are particularly important to a patient having a cap made, to be produced faithfully by the mould. Moulds embodying the invention can be made highly refractory and therefore suitable for moulding gold, e.g. for teeth, and for diecasting techniques, e.g. for zinc and aluminium. They can be used up to at least 1200°C. and, in the case of a 70% or 80% alumina content cement, up to about 1600°C. or, where the sand is replaced by a refractory aggregate, 2000°C.

It should be noted that, when large moulds are being formed, the mould composition can be applied to a former or other master article in the form of a fairly thin layer. Alternatively, wooden or other inserts can be used within the mould space to economise on the amound of mould composition required.

In some applications, it will be appropriate to use commercial accelerators. These can be included in the dry mix and/or added at the time of adding water.

In place of malachite, there may be used other refractory fillers or aggregates, through these should preferably have an inherent alumina content as this helps to strengthen and prevent shrinkage of the resulting mould. A possible example of such an aggregate or filler is crushed firebrick, though this has not yet been found commercially available in a fine enough grade to be suitable for the envisaged uses of embodiments of the present invention.

It is considered that the most useful embodiments of the present invention are those in which the maximum particle size is 300 microns, or even only 150 microns. It is possible that other properties of compositions embodying the invention may be useful without consideration of the coarseness of particles. In such a case, the particle size is immaterial. It might conveniently extent up to one millimetre. Also, there might be used fillers (e.g. lumps of stone) having much larger size, e.g. of the order of one or several centimetres, perhaps for use in the manner of the wooden inserts mentioned above.

CLAIMS

1. A composition comprising high alumina cement, aggregate and clay.

2. A composition as claimed in claim 1, in which the alumina content of the cement is present in a proportion from 39% to 80% w/w of the cement.

3. A composition as claimed in claim 2, in which the alumina content of the cement is present in a proportion substantially higher than 39% w/w of the cement.

4. A composition as claimed in claim 3, in which the alumina content of the cement is present in a proportion of at least 70% w/w of the cement.

5. A composition as claimed in claim 4, in which the alumina content of the cement is present in a proportion of about 80% w/w of the cement.

6. A composition as claimed in any preceding claim in which the cement is present in a proportion from 25% to 75% w/w.

7. A composition as claimed in claim 6, in which the cement is present in a proportion from 45% to 55% w/w.

8. A composition as claimed in any preceding claim, in which the clay is of commercial grade C.

9. A composition as claimed in any preceding claim, in which the clay is present in a proportion from 5% to 30% w/w.

10. A composition as claimed in claim 9, in which the clay is present in a proportion from 5% to 15% w/w.

11. A composition as claimed in any preceding claim, in which the clay is present in a proportion of substantially 5% w/w.

12. A composition as claimed in any preceding claim, in which the aggregate comprises sand.

13. A composition as claimed in claim 12, in which the sand is of 90—150 micron grade.

14. A composition as claimed in claim 12 or 13, in which the sand is present in a proportion from 5% to 70% w/w.

15. A composition as claimed in claim 14, in which the sand is present in a proportion from 15% to 40% w/w.

16. A composition as claimed in any one of claims 12 to 15, in which the sand and the cement together are present in a proportion of substantially 72.5% w/w.

17. A composition as claimed in claim 16, in which the sand is present in a proportion from 25% to 52.5% w/w.

18. A composition as claimed in any one of claims 1 to 11, comprising a refractory aggregate and no sand.

19. A composition as claimed in any one of claims 12 to 17, in which the aggregate further comprises a refractory aggregate.

20. A composition as claimed in 18 or 19, in which the refractory aggregate is malachite.

21. A composition as claimed in claim 20, in which the malachite is Malachite 200 of 75 micron grade.

22. A composition as claimed in any one of claims 18 to 21, in which the refractory aggregate is present in a proportion from 10% to 35% w/w.

23. A composition as claimed in claim 22, in which the refractory aggregate is present in a proportion from 15% to 30% w/w.

24. A composition as claimed in claim 23, in which the refractory aggregate is present in a proportion from 20% to 25% w/w.

25. A composition comprising substantially the following proportions w/w; 25% sand E, of 90—150 micron grade, 47.5% high alumina cement conforming to B.S. 915, 22.5% Malachite 200 of 75 micron grade and 5% clay of commercial grade C.

26. A composition as claimed in claim 25, in which the alumina content of the cement is present in a proportion from 70% to 80% w/w of the cement.

27. A composition as claimed in any preceding claim in combination with water.

28. A composition formed using 100 parts by weight of a composition as claimed in any one of claims 1 to 27 and from 10 to 50 parts by weight of water.

29. A composition as claimed in claim 28, formed using from 15 to 25 of the said parts of water.

30. A composition as claimed in claim 29, formed using substantially 20 of the said parts of water.

31. A method of making a mould in which a composition was claimed in any one of claims 27 to 30, is shaped as required and then allowed to dry.

32. A method as claimed in claim 31, including a step of drilling the mould after the drying.

33. A mould made by a method as claimed in claim 31 or 32.

34. A method of making an article in which there is used a mould as claimed in claim 33.

35. A method as claimed in claim 35, in which there is used with the mould a thermo-forming technique.

36. A method as claimed in claim 34, in which there is used with the mould a diecasting technique.

37. An article made using a method as claimed in claim 34, 35 or 36.

38. An article as claimed in claim 37, being a dental replacement.

39. A composition as claimed in any one of claims 1 to 30 formed into and used as a building material or building repair material.

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Suitable materials for use in the manufacture of vacuum moulds are epoxy resins. However, these are very expensive. As a substitute, there was tried what is called "ordinary Portland cement" but this proved technically unsuitable. There was then tried a simple mould material made of one part of cement and three parts of sand. Water was added at the time of mixing to give workability. The product was suitable in some respects but had the disadvantage of being unsuitable for drilling.

The inventor of the present invention discovered that the reason for this unsuitability was that the drill gouged out particles of sand and therefore removed more material than was required. He further discovered that this problem could be avoided by including in the mix a relatively soft material into which the drill could press peripheral particles of sand. In experiments, the best such matrix material he found (i.e. the one giving the best drilling properties in the resulting mould) was clay.

Thus according to one aspect of the invention there is provided a composition comprising high alumina cement, aggregate (e.g. sand) and a soft matrix material, preferably clay. The sand gives the material strength and helps to prevent shrinkage. The high alumina content of the cement produces a gel which lines the mould and produces a smoothness at the surface which makes for good reproduction. It also improves the refractory properties of the resulting mould.

The mix so formed is improved by adding to it a refractory aggregate. The best one found is malachite. This increases the temperature range of the resulting mould (which can be further increased by omitting some or all of the sand or other non-refractory aggregate) and appears to help substantially to prevent the mould from shrinking when being formed. It also reduces or prevents cracking at high temperatures. Other aggregates that were tried were (non-refractory) industrial talc and whiting (chalk) and more successfully (refractory) firebrick but these produced nothing like the improvement that was obtained with malachite.

The high alumina cement used is any one conforming to British Standard B.S. 915, which *inter alia* has an alumina content of at least 39% w/w. For high temperature work with the resulting mould it may be necessary to use a cement higher in alumina content than 39% and cement with an alumina content of 70% w/w or even 80% w/w have been used successfully.

The malachite is preferably one with a low iron content of about 0.75% w/w, a high inherent alumina content of around 40%—42% w/w and a small particle size of about 75 microns grade, such as is available for example under the trade name Malachite 200, 75 micron grade (made by English China Clays Limited) from Fordamin Company Sales Limited, No. 3 Wharf, Brighton Road, Shoreham-by-Sea.

The clay should be that known in the trade as Grade C or finer (the finer it is the dryer it can be made, which is considered to give better properties to the mix). 300 microns is about the maximum useful size on this basis and is preferred because finer grades, through dryer, are more expensive.

The sand can be anything less than 600 microns grade, preferably a 300 micron grade or, more preferably, what is commonly called 90—150 micron grade.

Useful mixes have been made up with the following proportions by weight: cement 25% to 75% though preferably 45% to 55%; sand 5% to 70%, though preferably 15% to 40%; clay 5% to 30%, though preferably 5% to 15%; and malachite, is used, 10% to 35%, better 15% to 30%, and preferably 20% to 25%. The properties of the mixes were found to be better in the preferred ranges. As an example, an optimum mix combining reasonable cost with good refractory properties and good resistance to shrinkage has the following composition w/w:—

25%	sand E, 90—150 micron grade.
47.5%	high alumina cement conforming to B.S. 915 with alumina content about 39%.
22.5%	Malachite 200, 75 micron grade.
5%	clay, grade C.

Almost as good mixes were obtained by varying inversely the proportions of cement and sand as far as 20% cement and 52.5% sand, the proportion in each case being about 72.5% of the two ingredients combined.

In making a mould out of the mix, water is added to cause the ingredients to adhere and the mix to set. The water also gives workability and placing ease (ease of removing air bubbles). The water also contributes to the final strength of the mould. For every 100 parts by weight of the mix there are required some 10 to 50 (preferably 15 to 25) parts by weight of water. The exact quantity will depend on the mix being used and the degree of workability. In the case of the example given above, a suitable quantity of water is 20 parts for 100 parts of mix.

The mould is produced and used in any suitable manner. For example, for a telephone casing, an internal form is made, e.g. by being carved out of wood, a sheet of plastic is vacuum formed over this and the wood removed, water is added to the mix according to the example given above and this is put into the plastic sheet in place of the wood, this hardens to form a mould from which the plastic sheet is removed and onto which plastic can be heat formed into telephone casings.

The only comparable moulding material at the moment is thought to be epoxy resin. Moulding materials embodying the invention are far cheaper than epoxy resin, are far easier to use because they do not stick to the hands, they are less dermatitic, they are non-toxic and can be disposed of easily without fear of degrading to give off toxic fumes, there is less wastage since it is not necessary to mix excessive quantities of two materials as is required with epoxy resins.

Moulds produced from compositions embodying the invention have a high resistance to shrinkage and good heat resistant properties. Such a composition is therefore highly suitable for use in the thermo-forming industry. However, it will be apparent that many other fields are open to it. For example, the composition can be used as a replacement for dental plaster. Its main advantage in this field is that the mould can be repeatedly used on high temperature work as it has good stability under repeated cycles of firing and being returned to ambient temperature. The material is particularly suitable for this purpose because of the excellent surface produced by the gel referred to above due to the high alumina cement. This allows small peculiarities of shape, which are particularly important to a patient having a cap made, to be produced faithfully by the mould. Moulds embodying the invention can be made highly refractory and therefore suitable for moulding gold, e.g. for teeth, and for diecasting techniques, e.g. for zinc and aluminium. They can be used up to at least 1200°C. and, in the case of a 70% or 80% alumina content cement, up to about 1500°C. or, where the sand is replaced by a refractory aggregate, 2000°C.

It should be noted that, when large moulds are being formed, the mould composition can be applied to a former or other master article in the form of a fairly thin layer. Alternatively, wooden or other inserts can be used within the mould space to economise on the amound of mould composition required.

In some applications, it will be appropriate to use commercial accelerators. These can be included in the dry mix and/or added at the time of adding water.

In place of malachite, there may be used other refractory fillers or aggregates, through these should preferably have an inherent alumina content as this helps to strengthen and prevent shrinkage of the resulting mould. A possible example of such an aggregate or filler is crushed firebrick, though this has not yet been found commercially available in a fine enough grade to be suitable for the envisaged uses of embodiments of the present invention.

It is considered that the most useful embodiments of the present invention are those in which the maximum particle size is 300 microns, or even only 150 microns. It is possible that other properties of compositions embodying the invention may be useful without consideration of the coarseness of particles. In such a case, the particle size is immaterial. It might conveniently extent up to one millimetre. Also, there might be used fillers (e.g. lumps of stone) having much larger size, e.g. of the order of one or several centimetres, perhaps for use in the manner of the wooden inserts mentioned above.

CLAIMS

1. A composition comprising high alumina cement, aggregate and clay.

2. A composition as claimed in claim 1, in which the alumina content of the cement is present in a proportion from 39% to 80% w/w of the cement.

3. A composition as claimed in claim 2, in which the alumina content of the cement is present in a proportion substantially higher than 39% w/w of the cement.

4. A composition as claimed in claim 3, in which the alumina content of the cement is present in a proportion of at least 70% w/w of the cement.

5. A composition as claimed in claim 4, in which the alumina content of the cement is present in a proportion of about 80% w/w of the cement.

6. A composition as claimed in any preceding claim in which the cement is present in a proportion from 25% to 75% w/w.

7. A composition as claimed in claim 6, in which the cement is present in a proportion from 45% to 55% w/w.

8. A composition as claimed in any preceding claim, in which the clay is of commercial grade C.

9. A composition as claimed in any preceding claim, in which the clay is present in a proportion from 5% to 30% w/w.

10. A composition as claimed in claim 9, in which the clay is present in a proportion from 5% to 15% w/w.

11. A composition as claimed in any preceding claim, in which the clay is present in a proportion of substantially 5% w/w.

12. A composition as claimed in any preceding claim, in which the aggregate comprises sand.

13. A composition as claimed in claim 12, in which the sand is of 90—150 micron grade.

14. A composition as claimed in claim 12 or 13, in which the sand is present in a proportion from 5% to 70% w/w.

15. A composition as claimed in claim 14, in which the sand is present in a proportion from 15% to 40% w/w.

16. A composition as claimed in any one of claims 12 to 15, in which the sand and the cement together are present in a proportion of substantially 72.5% w/w.

17. A composition as claimed in claim 16, in which the sand is present in a proportion from 25% to 52.5% w/w.

18. A composition as claimed in any one of claims 1 to 11, comprising a refractory aggregate and no sand.

19. A composition as claimed in any one of claims 12 to 17, in which the aggregate further comprises a refractory aggregate.

20. A composition as claimed in 18 or 19, in which the refractory aggregate is malachite.

21. A composition as claimed in claim 20, in which the malachite is Malachite 200 of 75 micron grade.

22. A composition as claimed in any one of claims 18 to 21, in which the refractory aggregate is present in a proportion from 10% to 35% w/w.

23. A composition as claimed in claim 22, in which the refractory aggregate is present in a proportion from 15% to 30% w/w.

24. A composition as claimed in claim 23, in which the refractory aggregate is present in a proportion from 20% to 25% w/w.

25. A composition comprising substantially the following proportions w/w; 25% sand E, of 90—150 micron grade, 47.5% high alumina cement conforming to B.S. 915, 22.5% Malachite 200 of 75 micron grade and 5% clay of commercial grade C.

26. A composition as claimed in claim 25, in which the alumina content of the cement is present in a proportion from 70% to 80% w/w of the cement.

27. A composition as claimed in any preceding claim in combination with water.

28. A composition formed using 100 parts by weight of a composition as claimed in any one of claims 1 to 27 and from 10 to 50 parts by weight of water.

29. A composition as claimed in claim 28, formed using from 15 to 25 of the said parts of water.

30. A composition as claimed in claim 29, formed using substantially 20 of the said parts of water.

31. A method of making a mould in which a composition was claimed in any one of claims 27 to 30, is shaped as required and then allowed to dry.

32. A method as claimed in claim 31, including a step of drilling the mould after the drying.

33. A mould made by a method as claimed in claim 31 or 32.

34. A method of making an article in which there is used a mould as claimed in claim 33.

35. A method as claimed in claim 35, in which there is used with the mould a thermo-forming technique.

36. A method as claimed in claim 34, in which there is used with the mould a diecasting technique.

37. An article made using a method as claimed in claim 34, 35 or 36.

38. An article as claimed in claim 37, being a dental replacement.

39. A composition as claimed in any one of claims 1 to 30 formed into and used as a building material or building repair material.

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